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MELAMINE BARBITURATE CRYSTAL TWINNING AS A FUNCTION OF TEMPERATURE*

Supramolecular assemblies are the intermediate stage between biological and chemical systems. Their structure consists of compounds held together by the hydrogen bonding like DNA, but they are more predictable like common chemical molecules [1].

Most of the supramolecular assemblies provide host-function for incapsulated molecules. One supposed that oxygen radicals also turn into guest-molecules in some cases like melamine barbiturate [2]. Melamine links barbituric acid into a rosette by distributed hydrogen bonding, and thin two-dimensional layers are bind by hydrophobic bonds. The layers are hexagonal which every molecule has a triple hydrogen bond in. Excluding these two bonding types there are also planes linked by electrostatic bonds.

Thus, melamine barbiturate is extremely stable in wild range of pH and has highly crystallinity about 88 % to 90 % due to the synthetic method [3]. The assembly stability is in dependance on the protonation/deprotonation of the individual compound. Therefore, in case of barbituric acid deprotonation process melamine barbiturate disassembles.

Melamine barbiturate crystals have highly specific morphology. The assembly forms 8-pointed star-shaped aggregates that are polycrystalline (Fig. 1A).

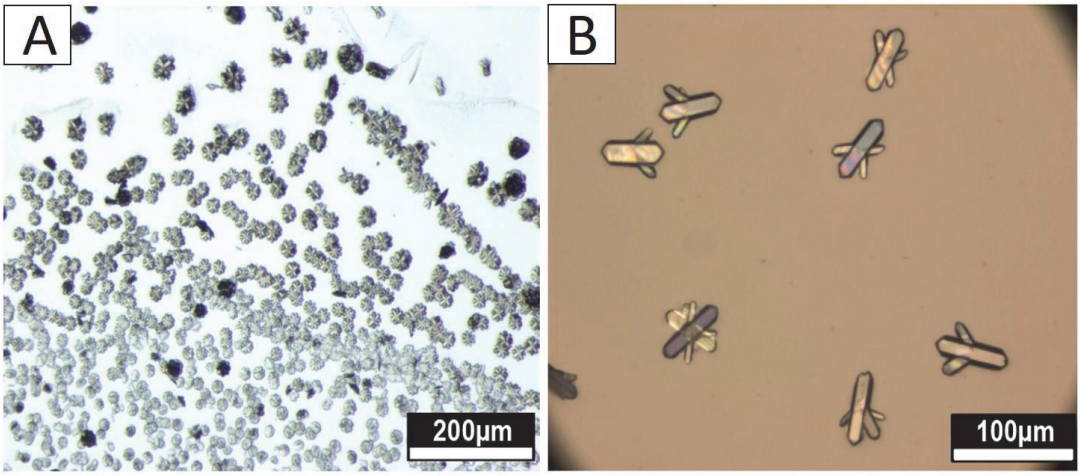

Fig. 1. A – Melamine barbiturate from water solution; B – particles achieved by diffusion-controlled formation process

The particles size is in range from 20 µm to 100 µm, and no cleavage is observed. A synthesis method does not affect the edges of the particles that are constantly smooth but has a high impact in case of a monocrystal formation (Fig. 2B).

There is no additional melamine or barbituric acid molecules restructuration before reaction starts. Thus, the reaction has neither kinetics no thermodynamic limitation at all. After the nucleating seed appears, the reaction is limited only by diffusion process of individual components to the seed surface.

In case of diffusion-controlled formation process there is a weak twinning effect. The synthetic scheme requires a mixing absence to decrease components diffusion rate.

One observed that there is a difference in the twinning effect in due to formation process temperature. The defect intensity enhances dependently on the temperature increasing (Fig. 2 A-I). This is reasonable due to the extended component diffusion to the nucleating seed surface. Thereafter, crystals form pronouncedly faster but with highly twinning.

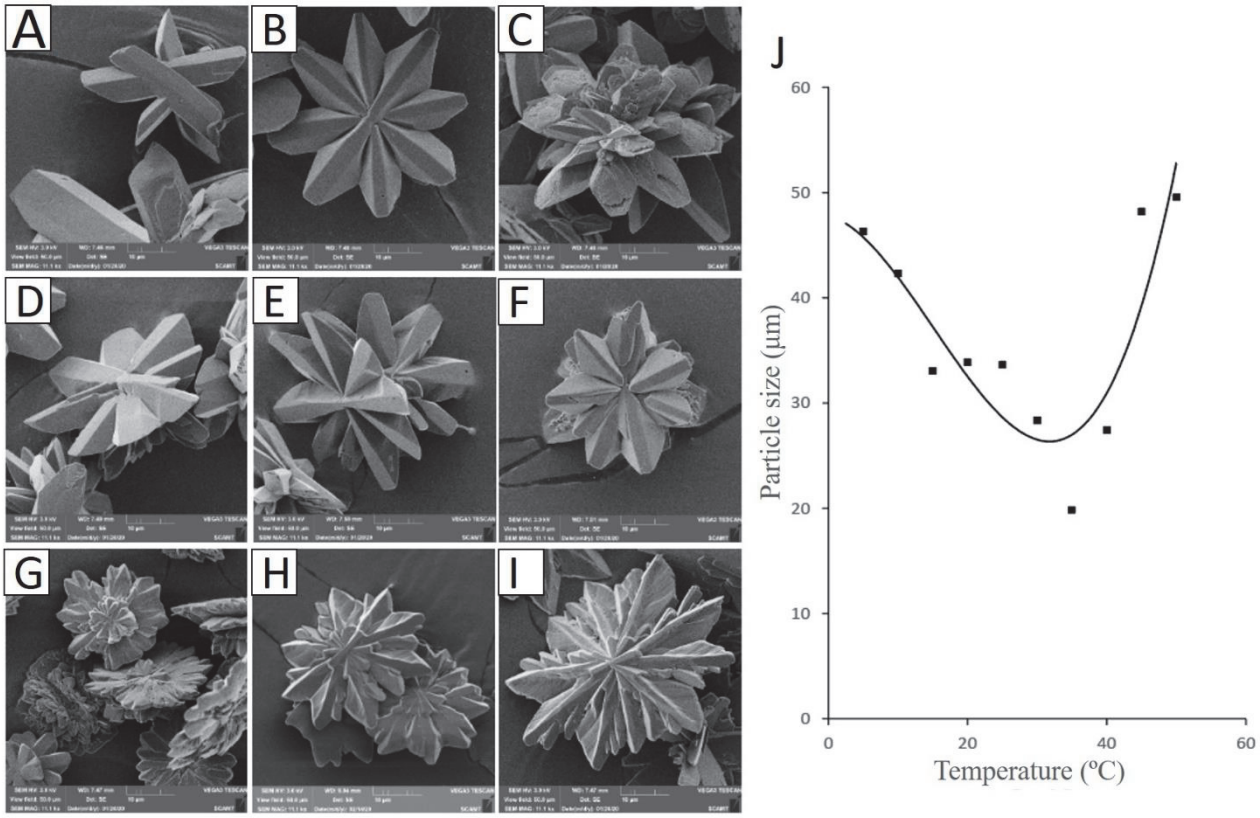

Fig. 2. Melamine barbiturate particle morphology in dependance on the formation temperature (A – 5 °C, B – 10 °C, I – 45 °C); K – size distribution as a temperature function

For the supramolecular assemblies there is no high reaction heat effect observed before due to the almost low binding energies, although the temperature impacts. The nucleation process is in accordance with Arrhenius equation, so the heat motion provides higher diffusion rate.

The twinning intensity is supposed to be in dependance on real concentration and the equilibrium concentration ratio in the specific formation point [4]. Accordingly, the nucleation point provides the highest concentration, thus there is the twinning effect only in the center of the aggregate at the low temperatures. The temperature increasing leads to the multiple twinning effect on the crystal tails due to the diffusion enhancement of the components.

It was also shown that the size of aggregates of melamine barbiturate depends on the temperature also. The obtained correlation function has a minimum at the temperature about 36–38 °C (Fig. 2J).

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